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LUBRICITY OF JET FUELS

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LUBRICITY PROPERTIES OF HIGH-TEMPERATURE JET FUELS

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TABLE OF CONTENTS

		Page
I.	INTRODUCTION	1
II.	METALLURGY STUDIES WITH JET FUELS	2
	A. Additional Studies On K-Monel	2
	B. Softened Steel	8
	C. Silver-On-Silver	17
III.	SCUFFING OF STEEL	21
	1. Lubricity Additives	21
	2. Sulfur Compounds	23
	3. Olefins	29
IV.	PUBLICATIONS	34
V.	FUTURE WORK	35

FOREWORD

This report was prepared by the Advanced Lubrication Project, Products Research Division, Esso Research and Engineering Co. at Linden, N.J. under Contract AF33(615)2828. This program is administered by the Air Force Aero Command with Arthur F. Levenstein, Capt., USAF as coordinator.

This report covers work conducted from 15 November, 1967 to 15 February, 1968.

ABSTRACT

New information has been obtained on the importance of metallurgy and the mechanism of scuffing.

K-Monel, a softer and less corrodible metal than steel, has shown some unusual behavior. Unlike steel, it scuffs at low loads, particularly if neither oxygen or water are present. Unlike steel, the addition of a corrosion inhibitor increases scuffing of K-Monel. Soft steel also behaves differently from hard steel. With a highly-refined fuel, scuffing is more severe in dry argon than in wet air, whereas the opposite order had been found on hard steel. These effects are not understood.

Mixtures of methylnaphthalene in paraffinic fuels are effective antiwear, antiscuff fuels in all atmospheres and with all metals, including K-Monel and silver.

Additives that are good antiwear agents are also good antiscuff agents but larger concentrations are required for good scuff control. Sulfur compounds are not effective antiscuff agents in air, confirming that they are not the lubricity compounds in conventionally refined fuels. Olefins that are unstable to oxidation tend to improve the antiwear, antiscuff properties. Their removal in the refining process probably is partly responsible for the decrease in lubricity.

Two additional papers have been prepared for publication.

I. INTRODUCTION

In the previous report the study of the lubricity of jet fuels was extended to two new areas: scuffing and other metallurgies.

Scuffing is a different phenomenon from wear and certain differences were noted in the effect of test variables: 1) Scuffing is more severe in dry inert atmospheres and with softer, corrosion-resistant metals. 2) Certain additives, such as ZnDDP, which are effective antiwear compounds at 40ppm, are not good antiscuff compounds. 3) Sulfur compounds, which had not shown any antiwear behavior, did show some antiscuff activity.

These studies have been continued, and more definitive conclusions have been reached concerning the nature of scuffing and the effect of additives and sulfur compounds. In addition the effect of oxidation-sensitive hydrocarbons has been studied using various olefins.

The study of other metallurgies was started for two reasons: 1) to clarify the mechanism of corrosive wear and also of scuffing. 2) to see which of the conclusions found with steel will hold generally, and which will be specific for steel. The work reported herein, although confirming many previous conclusions, shows many puzzling aspects, and points out the need for further work in this area.

II. METALLURGY STUDIES WITH JET FUELS

In the previous quarterly report, it was shown that several non-corrodible metals (e.g., K-Monel, stainless steel Type 302) were more easily scuffed than 52100 steel. Metallurgy studies have been continued along the following lines: (a) additional K-Monel studies, (b) AISI 52100 steel equal to K-Monel in hardness, and (c) silver, another corrosion resistant metal. The data to be presented show many anomalous and unexplained phenomena. However, a complete discussion of the data will be delayed until the next report when additional results are available.

A. Additional Studies On K-Monel

Previously, it had been found that K-Monel, although a non-corrodible metal, was easily scuffed at low loads, especially in dry argon. Work has continued along the lines of wet argon and dry air atmospheres, additive effects, and studies at 160F.

Tests with K-Monel using Bayol 35 and RAF-176-64 are shown in Tables 1 and 2, respectively. As may be seen, for both the highly-refined fuel (Bayol 35) and the conventionally-refined fuel (RAF-176-64), the presence of moisture improves the scuff resistance of K-Monel. Oxygen also reduces the scuffing tendency but not as effectively as moisture. In Figure 1 a comparison of Bayol 35 and RAF-176-64 on K-Monel for wet argon and wet air is shown. In wet argon the results agree with previous steel-on-steel data. In wet air, however, RAF-176-64 scuffs more readily than Bayol 35. The reason for the reversal in wet air is not understood at this time.

Additional work was done concerning the effectiveness of additives on K-Monel in four atmospheres: dry and wet (saturated) argon, dry and wet air. The results are shown in Table 3. Previous results are included for completeness. It can be seen that oleic acid is a pro-scuff agent in wet argon as well as in wet air. In dry air oleic acid is a pro-wear agent although it does not scuff any more easily than the base fluid itself.

As found for dry argon, ER-3 is an effective antiscuff agent in dry air also. Both ER-3 and oleic acid were previously found to be good antiscuff additives on steel (see Quarterly Report Nos. 9 and 10). However, of the two only ER-3 was effective on K-Monel.

The results with tricresyl phosphate (TCP) were quite varying. In dry argon, TCP acted as an antiscuff additive. In the presence of moisture, TCP acted like oleic acid in that it promotes scuffing. It is well-known that TCP can undergo hydrolysis to form the free acid. This acid may cause scuffing in a manner similar to oleic acid. In dry air, TCP, like oleic acid, shows slight pro-wear effects.

Other additives in Table 3 vary in effectiveness depending upon atmosphere. ER-1 showed antiwear effects in wet argon while controlling scuffing at 3kg in dry air. On the other hand, ER-4 was ineffective.

Several tests were run at 160F using K-Monel as shown in Table 4. The

TABLE 1

4-BALL TESTS: K-MONEL

(1200rpm, 15min, 74F, Bayol 35)

Load, kg:	Wear Scar Diameter, mm							
	1	1.5	2	3	4	5	7	10
Dry Argon	*	-	*	*	-	-	-	-
Wet Argon	0.48	-	0.53	0.54	*	*	-	-
Dry Air	0.40	0.43	0.45, *	*	-	-	-	-
Wet Air	0.51	-	-	0.58	0.54	0.57	0.61	0.61

Load, kg:	Coefficient Of Friction							
	1	1.5	2	3	4	5	7	10
Dry Argon	0.77**	-	0.51**	0.57**	-	-	-	-
Wet Argon	0.08	-	0.11	0.10	**	Off Scale	-	-
Dry Air	0.10	0.14	0.13, **	**	-	-	-	-
Wet Air	0.16	-	-	0.12	0.14	0.13	0.13	0.09

* Scuffed
** Friction erratic

TABLE 2

4-BALL TESTS: K-MONEL

(1200rpm, 15min, 74F, RAF-176-64)

	Wear Scar Diameter			
Load, kg:	1	3	5	7
Dry Argon	*	*	-	-
Wet Argon	0.40	0.42	0.43	*
Dry Air	0.48	*	-	-
Wet Air	0.55	0.61	0.63	*

	Coefficient Of Friction			
Load, kg:	1	3	5	7
Dry Argon	0.85**	0.93**	-	-
Wet Argon	0.25	0.08	0.07	0.60**
Dry Air	0.12	0.91**	-	-
Wet Air	0.12	0.12	0.11	Off Scale

* Scuffed
** Friction erratic

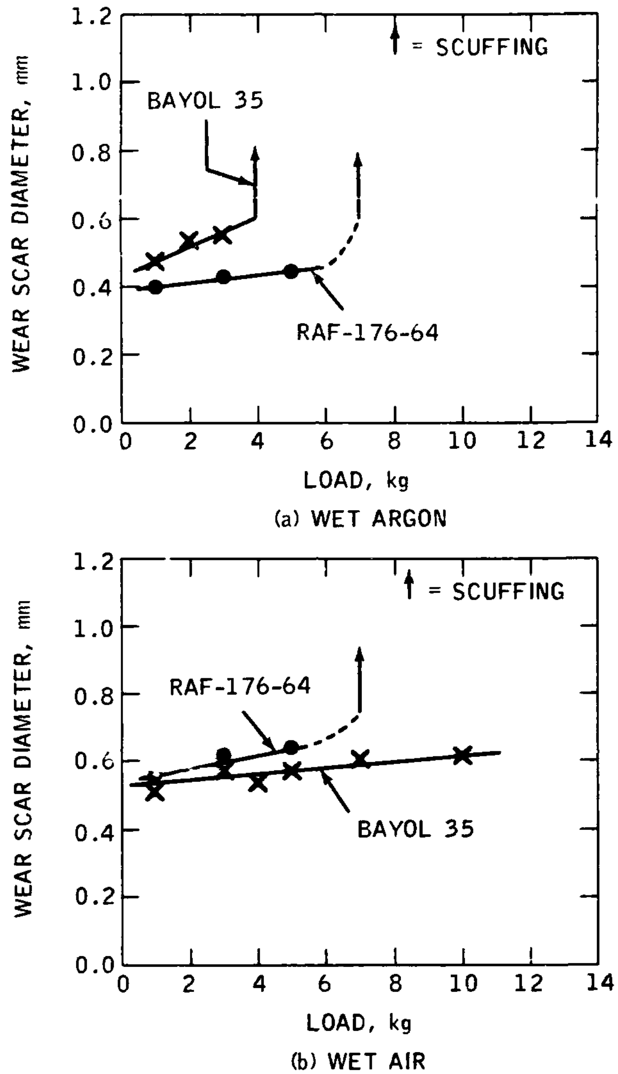


FIGURE 1 - COMPARISON OF BAYOL 35 WITH RAF-176-64 ON K-MONEL (FOUR BALL TESTS - 1200RPM, 15MIN, 77F)

TABLE 3

EFFECT OF LUBRICITY ADDITIVES ON K-MONEL

(4-Ball Test, 1200rpm, 15min, 74F)

	Wear Scar Diameter, mm										
	Dry Argon		Wet Argon			Dry Air			Wet Air		
Load, kg:	1	3	1	3	5	1	3	5	1	3	5
Wt.% Additive In Bayol 35											
None	*	*	0.48	0.54	*	0.40	*	-	0.51	0.58	0.57
0.1 Oleic Acid	*	*	*	-	-	0.60	*	-	0.55	*	-
0.1 TCP	0.35	*	0.45	*	-	0.62	*	-	0.43	0.55	*
0.1 ER-1	-	*	0.36	0.37	*	0.35	0.41	*	-	0.54	-
0.1 ER-3	0.36	0.43	0.42	0.48	*	0.45	0.50	*	0.50	0.60	-
0.1 ER-4	-	*	-	-	-	-	-	-	-	0.53	-

* Scuffing

TABLE 4

EFFECT OF BASE FUEL AND CONDENSED RING AROMATICS AT 160F ON K-MONEL

(4-Ball Tests, 1200rpm, 15min, 1 kg)

Fuel	Wear Scar Diameter, mm			
	Dry Argon	Wet Argon	Dry Air	Wet Air
Bayol 35	*	*	0.38	0.34
RAF-176-64	*	*	0.39	-
5% 1-methylnaphthalene in Bayol 35	*	0.33	0.42	-
30% 1-methylnaphthalene in Bayol 35	0.31	0.35	0.32	-
30% Indene in Bayol 35	0.48	0.40	0.29	-

* Scuffed

two base fuels, Bayol 35 and RAF-176-64, are shown in the table along with data on two condensed-ring aromatic blends in Bayol 35, 1-methylnaphthalene and indene. In argon (wet and dry) both base fuels scuffed even at a low load of 1 kg. Apparently, the higher temperature offsets the effect of water to prevent scuffing in wet argon. In air, scuffing did not occur and the wear was not too great. Data at two temperatures are shown in Figure 2. Oxidation of the fuel at 160F probably accounts for the reduced wear at the higher temperature, especially in wet air.

The effect of condensed-ring aromatics at 160F is shown also in Table 4. Both 1-methylnaphthalene and indene are very effective as antiscuff agents. This is in agreement with earlier data at 74F. Table 4 also shows that indene exhibits high antiwear activity in dry air.

Several lubricity additives were tested at 160F (Table 5). At this temperature, ER-3 continued to act as a very good antiscuff agent. Even 50ppm ER-3 was effective. Oleic acid, on the other hand, exhibited the same behavior at 160F as it did at 74F. Not only did oleic acid fail to prevent scuffing in dry and wet argon, but it caused scuffing and increased wear in wet and dry air respectively. ER-1 was ineffective in all atmospheres as shown in Table 5.

To summarize, K-Monel scuffs very easily under four-ball test conditions, especially in a dry, inert atmosphere. However, both air and especially moisture have antiscuffing effects. Additives vary in effectiveness: ER-3 is a very good antiscuff agent at 74F and 160F while oleic acid shows adverse effects. Synergism of condensed-ring aromatics in Bayol 35 found with steel holds also for K-Monel.

B. Softened Steel

Tests were carried out using AISI 52100 steel balls which had been softened by heat-treatment. Thus, K-Monel data could be compared directly to that of steel having the same hardness. Typical hardness values are shown below:

	K-Monel	Softened 52100
Rockwell R_c	27	25

A series of Four-Ball tests were run with the soft steel using Bayol 35 and RAF-176-64. The results are shown in Figures 3 to 6. A summary of the scuffing loads obtained in all four atmospheres is shown in Table 6. In dry argon, results agree with previous data on hard steel: a highly-refined fuel (Bayol 35) scuffs more easily than a conventionally-refined fuel (RAF-176-64). However, in going from dry argon to wet air soft steel behaves quite differently from hard steel. As seen in Table 6, Bayol 35 scuffs in the sequence wet air > dry air > wet argon > dry argon, where the order represents the relative magnitude of the scuff load in the indicated atmosphere. The reverse order was found for RAF-176-64. Apparently, for soft steel corrosive wear improves the scuff resistance. Oxides formed may not be too abrasive toward the soft steel surface, and these oxides could keep the asperities apart and thereby prevent scuffing. It is a mystery at this point why RAF-176-64 scuffs more readily in wet air than in dry argon.

The effect of 1-methylnaphthalene and 1-methylnaphthalene in Bayol 35 on lubricity for the softened steel is shown in Table 7. The unusual synergism found previously with 1-methylnaphthalene in Bayol 35 is clearly not shown here. As the

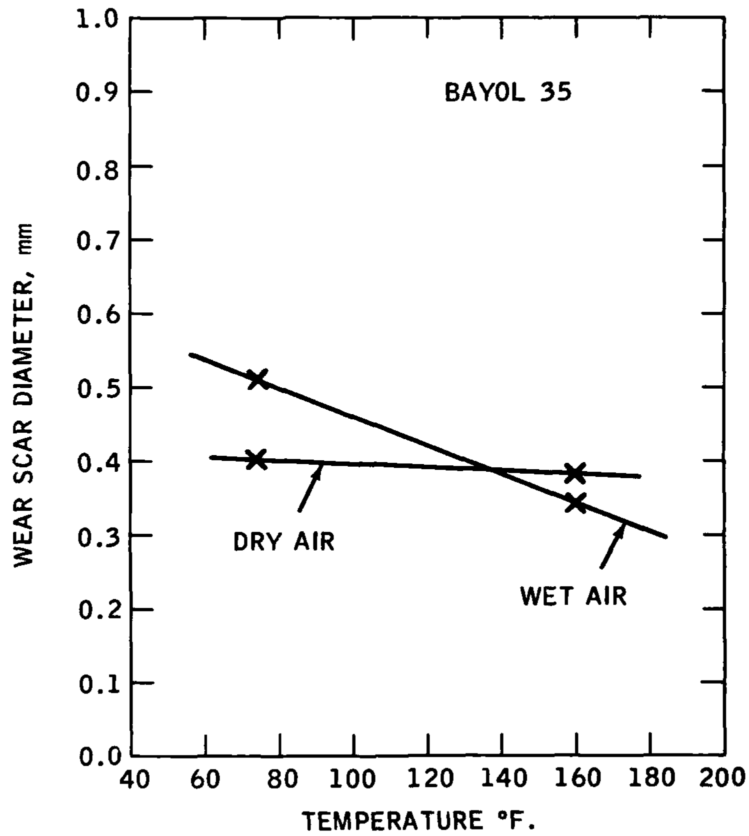


FIGURE 2 - EFFECT OF TEMPERATURE ON K-MONEL WEAR (FOUR BALL TESTS - 1200RPM, 15MIN, 1 KG)

TABLE 5

EFFECT OF LUBRICITY ADDITIVES AT 160F ON K-MONEL

(4-Ball Tests, 1200rpm, 15min, 1 kg)

Wt.% Additive In Bayol 35 (ppm)	Wear Scar Diameter, mm			
	Dry Argon	Wet Argon	Dry Air	Wet Air
None	*	*	0.38	0.34
0.1 ER-3 (1000)	0.53	0.43	0.43	0.38
0.005 ER-3 (50)	0.30	0.46	0.34	-
0.1 ER-1 (1000)	*	*	0.36	0.33
0.1 Oleic Acid (1000)	*	*	0.67	*

* Scuffing

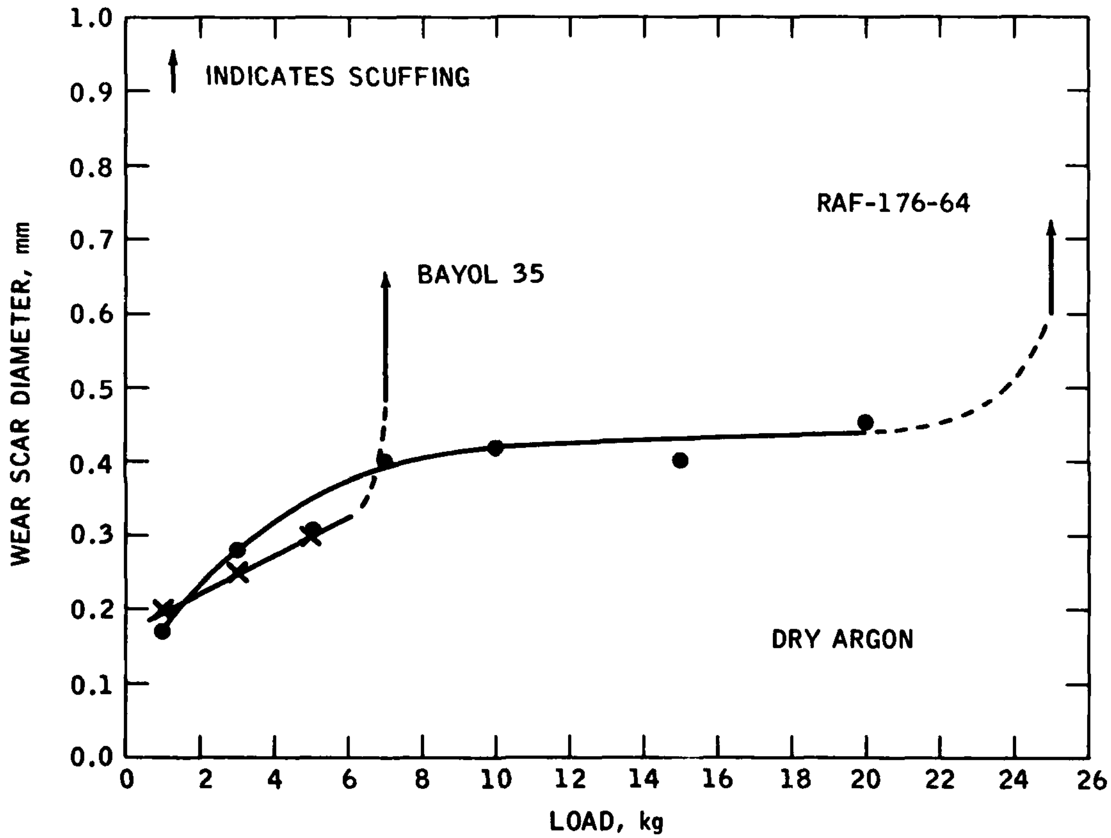


FIGURE 3 - FUEL TYPE AFFECTS WEAR AND SCUFFING (FOUR BALL TESTS - 1200RPM, 15MIN, 74F, R_c 25 STEEL)

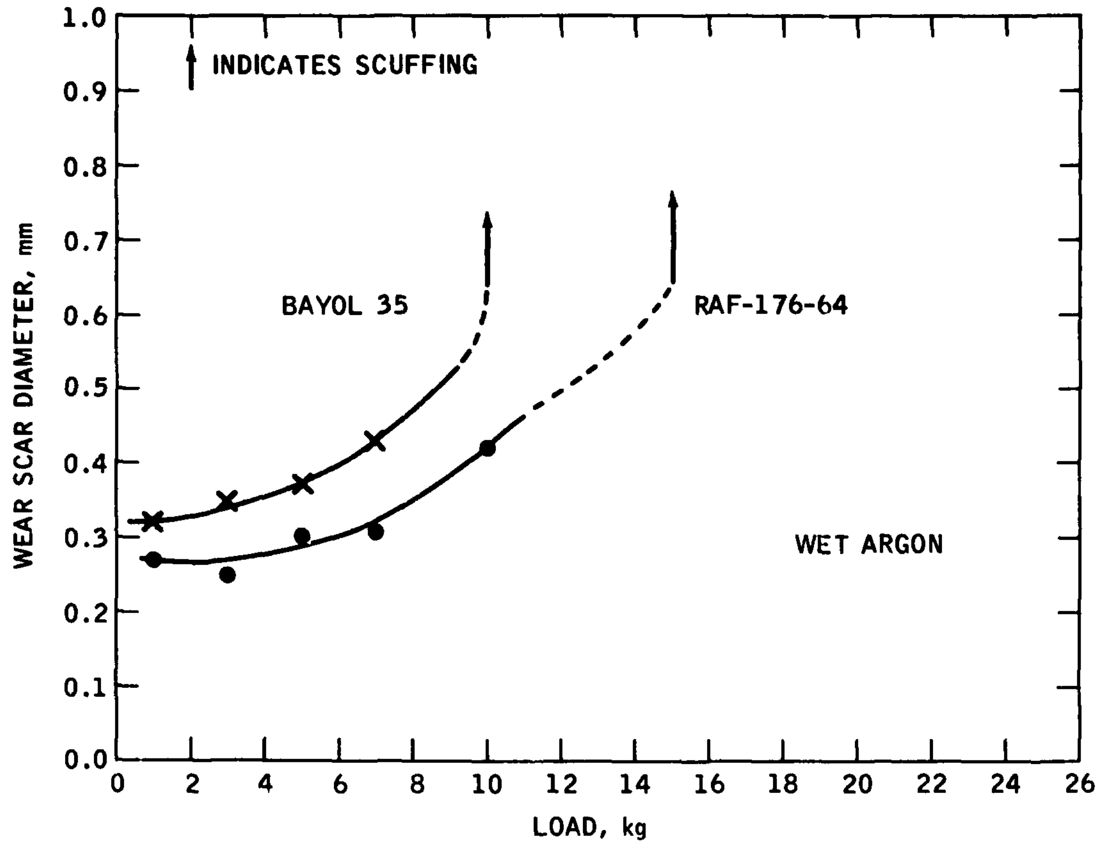


FIGURE 4 - FUEL TYPE AFFECTS WEAR AND SCUFFING (FOUR BALL TESTS - 1200RPM, 15MIN, 74F, R_c 25 STEEL

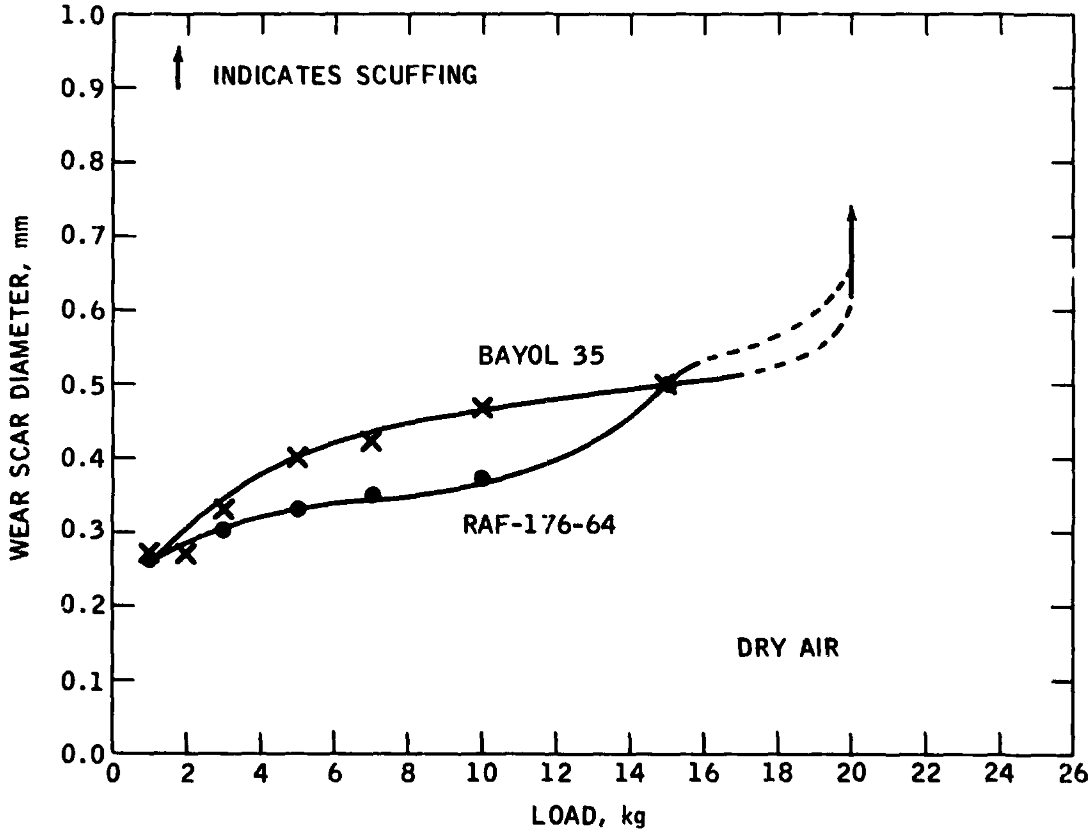


FIGURE 5 - FUEL TYPE AFFECTS WEAR AND SCUFFING (FOUR BALL TESTS - 1200RPM, 15MIN, 74F, R_c 25 STEEL)

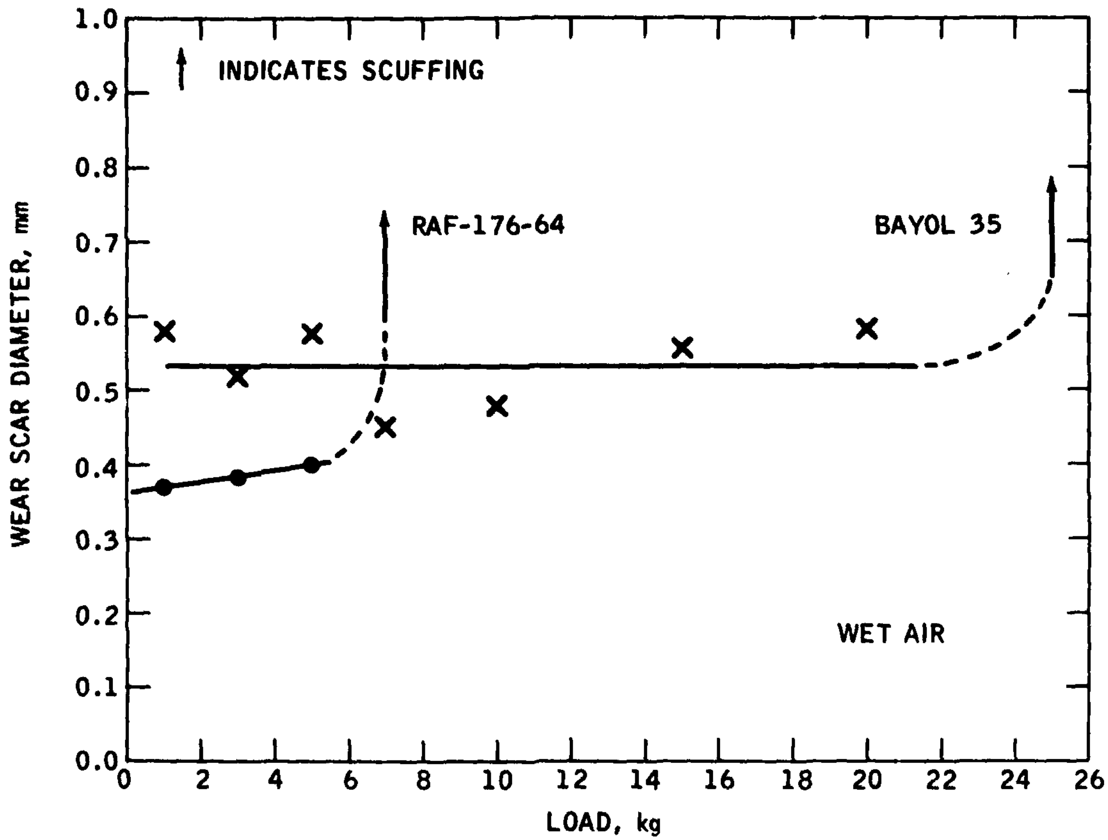


FIGURE 6 - FUEL TYPE AFFECTS WEAR AND SCUFFING (FOUR BALL TESTS - 1200RPM, 15MIN, 74F, R_c 25 STEEL)

TABLE 6

SCUFFING LOADS IN VARIOUS ATMOSPHERES

(4-Ball Tests, 1200rpm, 15min, 74F)

Metal: 52100 Steel (R_c 25)

	Scuffing Load, kg			
	Dry Argon	Wet Argon	Dry Air	Wet Air
Bayol 35	6-7	8-10	16-20	21-25
RAF-176-64	21-25	11-15	16-20	6-7

TABLE 7

COMPARISON OF BAYOL 35 AND
1-METHYLNAPHTHALENE ON 25 R_c STEEL

(4-Ball Tests, 1200rpm, 15min, 74F 1 kg)

	Wear Scar Diameter, mm			
	Dry Argon	Wet Argon	Dry Air	Wet Air
Bayol 35	0.20	0.32	0.27	0.58
30% 1-methylnaphthalene in Bayol 35	0.30	0.35	0.26	0.37
1-methylnaphthalene	0.25	0.27	0.24	0.40

wear scars indicate, conditions were probably too mild for any synergism to show up.

C. Silver-On-Silver

Even with a metal such as K-Monel, a limited amount of oxide formation or corrosion might occur in a sliding system where fresh metal is constantly being exposed. For this reason, work was done using silver as the sliding metal. For this study, silver-plated steel balls were employed. In order to avoid the problem of breaking through the silver coating as had previously occurred with gold-coated balls (see Quarterly Report No. 10), a plating thickness of 0.05 inch was employed. After all tests, examination of the wear scars indicated that the silver coat had not been broken through.

Four-Ball tests of silver-on-silver were run using Bayol 35 and RAF-176-64. Test conditions were 1200rpm, 15min, 74F and air and argon (wet and dry) atmospheres. At the lowest Four-Ball load of 1 kg, severe scuffing occurred with both fuels in all four atmospheres. Figure 7 shows a wear scar, characteristic of these silver-on-silver tests. Metal welding and severe damage are evident. Silver does not readily form an oxide coat. Thus, the absence of any surface film probably accounts for silver's low scuff resistance.

Synergism was found when 1-methylnaphthalene was added to Bayol 35 and tested on silver. In all four atmospheres scuffing was eliminated by adding 30% aromatic to Bayol 35. On the other hand, tests with 1-methylnaphthalene itself failed by scuffing in all four atmospheres. The wear scars for the 30% mixtures are shown below:

Silver-On-Silver WSD (mm)

(1200rpm, 1 kg, 15min, 74F)

Dry Argon	0.78
Wet Argon	0.87
Dry Air	0.70
Wet Air	0.65

Although the wear scars may seem slightly high, no scuffing occurred. Friction traces were smooth and tests were quiet. Thus, the synergistic behavior of the aromatic is clearly not limited to a particular metallurgy or atmosphere.

Several additives were tested to determine their effectiveness as anti-scuff agents on silver. Table 8 shows the results. ER-3 was the most universal of the four tested -- it eliminated scuffing in all four atmospheres. Oleic acid and TCP were both effective only in air (dry and wet). Both were more effective, i.e., less wear, in wet air than dry air. These data illustrate that additives vary in their effectiveness depending on the specific metallurgy employed. In wet air, both oleic acid and TCP acted as pro-scuff agents on K-Monel. However, they are quite effective in wet air on silver. ZnDDP was effective as an antiscuff agent in three out of the four atmospheres -- it was ineffective in dry argon. It is surprising that ZnDDP is even effective in any atmosphere since it contains sulfur, and it is well-known that sulfur can violently attack silver.

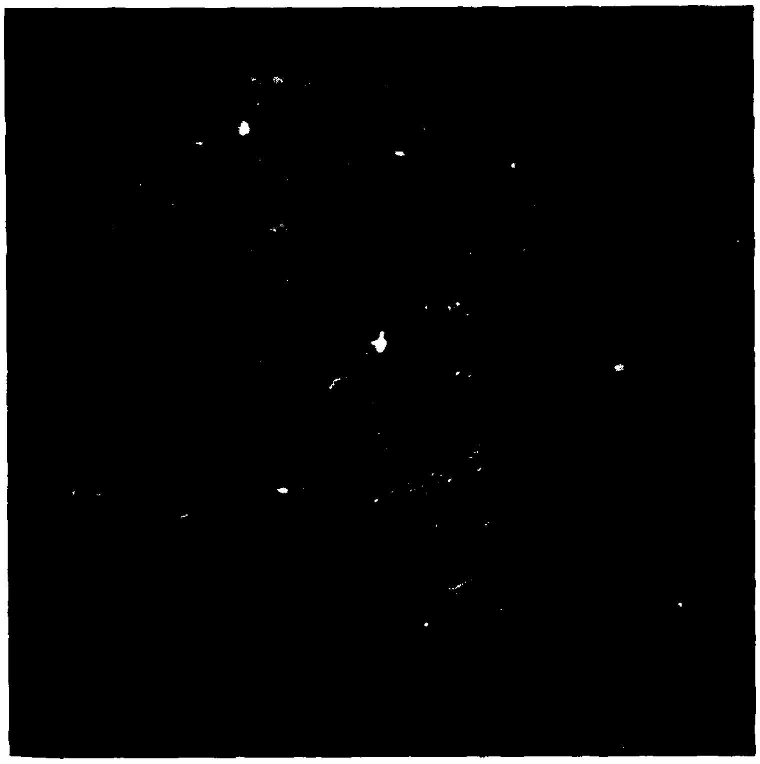


FIGURE 7 - SCUFFING ON SILVER SPECIMEN
(FOUR-BALL TEST: BAYOL 35, 1 KG,
1200RPM, 15MIN, 77F, WET ARGON)

= 1.0 mm

TABLE 8

EFFECT OF ADDITIVES AS ANTISCUFF AGENTS ON SILVER

(4-Ball Test, 1200rpm, 15min, 74F, 1 kg)

% Additive In Bayol 35	Wear Scar Diameter, mm			
	Dry Argon	Wet Argon	Dry Air	Wet Air
None	*	*	*	*
0.1 ER-3	0.73	0.70	0.93	0.95
0.1 Oleic Acid	*	*	1.17	0.93
0.1 ZnDDP	*	1.30	0.80	0.73
0.1 TCP	*	*	0.85	0.67

* Scuffing

Summarizing, ER-3 was effective in all four atmospheres. The other additives -- oleic acid, TCP, ZnDDP -- were effective in wet and dry air, but not in dry argon. ZnDDP showed an effect in wet argon; oleic acid and TCP did not. These results are in complete agreement with previous findings on steel scuffing in that ER-3 was the most effective of the additives tested.

III. SCUFFING OF STEEL

In the previous report, studies were reported on scuffing, a mechanism distinct from normal wear. Lubricity additives at 50ppm (a concentration high enough to prevent corrosive wear) were for the most part ineffective in preventing scuffing.

This work has now been extended to higher concentrations of additives and also to the effect of sulfur compounds and olefins. The principal conclusions are: 1) higher concentrations of additives increase the scuff load, 2) sulfur compounds are ineffective in air, 3) unstable olefins give higher scuffing loads.

1. Lubricity Additives

Scuff loads were obtained using the 4-ball machine. Various additives were examined at different concentrations in PW-523, a highly-refined jet fuel. The data at 1000ppm concentration are presented in Table 9, and are summarized below, along with previously reported data at 50ppm.

Four-Ball Scuff Load, kg

	Dry Argon		Wet Air	
Additives	50ppm	1000ppm	50ppm	1000ppm
None	1		0.5	
ZnDDP	2	10	2	20
Oleic Acid	3	10	20	> 30
ER-1	2	10	3	15
ER-3	5	30	20	> 30

It will be noted that all the additives are more effective in wet air than in dry argon. This is believed to be a reflection of the natural tendency of all oils or fuels to scuff less if oxygen and water are present. Both oxygen and water form oxides, which reduce adhesion and scuffing. In addition, the simple adsorption of water also tends to diminish scuffing. The reason that non-additive fuels scuff more readily in wet air is that corrosive wear plays an important part in the scuffing process: the presence of oxygen and water causes the formation of iron oxide which in turn causes abrasive wear and scuffing. The lubricity additives suppress corrosive wear and thus allow water and oxygen to fulfill their antiscuff function. Also, the additives themselves are more reactive with the surface when a full oxide layer is present.

A second important fact from the above table is that the scuff load increases as the concentration increases. This is different from the case of corrosive wear, where only 50ppm was usually sufficient to eliminate the wear, and

TABLE 9

EFFECT OF LUBRICITY ADDITIVES ON WEAR

(Four-Ball Tests, 1200rpm, 240F, 15min)

	Wear Scar Diameter, mm												Coefficient Of Friction											
	Dry Argon						Wet Air						Dry Argon						Wet Air					
Load, kg:	3	5	10	15	20	30	3	10	15	20	25	30	3	5	10	15	20	30	3	10	15	20	25	30
% Additive In FW-523*																								
0.1% ZnDDP	0.23	0.26	S**	-	-	-	0.37	0.38	0.65	S**	-	-	0.09	0.09	****	-	-	-	0.18	0.16	0.12	****	-	-
0.1% Oleic Acid	0.27	0.30	0.83	S**	-	-	0.26	0.44	0.39	-	0.48	0.51	0.11	0.08	***	****	-	-	0.14	0.08	0.08	-	0.10	0.12
0.1% ER-1	0.25	0.27	S**	-	-	-	0.48	0.63	S**	-	-	-	0.09	0.13	****	-	-	-	0.16	0.19	****	-	-	-
0.1% ER-3	0.34	-	0.42	0.39	0.38	0.62	0.33	0.38	0.36	-	0.53	0.52	0.06	-	0.08	0.09	0.10	0.11	0.10	0.13	0.11	-	0.13	0.12

* FW-523 scuffed at 1 kg in argon and 0.5 kg in wet air.
** "S" indicates seizure.
*** Erratic friction and chattering noise.
**** Friction off-scale.

further increases in concentration had little effect. Again this is not surprising: scuffing is a dynamic condition in which the surface layer is continuously rubbed off and must reform before the next traverse. Higher loads cause the surface layers to be rubbed off faster, and this must be countered by a faster film formation, i.e. a higher concentration of additive available at the surface to react.

Both of these facts are illustrated in Figures 8 and 9 which show the complete data for ER-3. In dry argon 50ppm ER-3 is only effective up to 3kg, whereas in wet air it is effective up to 15kg. Increasing the concentration to 1000ppm increases the scuff load in both dry argon and wet air.

The implication of these data to the actual case of jet fuel systems in aircraft is this: if the problem is one of simple adhesion (sticking) then only a few ppm of additive should be required to eliminate it. However, if the problem is one of galling (as in slipper pads) then a higher concentration of additive is necessary. As already noted, metallurgies that are softer or more corrosion resistant are more subject to galling and therefore will require more additive to stay out of trouble.

2. Sulfur Compounds

Previous ball-on-cylinder tests indicated that some sulfur compounds, although they had little antiwear effect, might reduce scuffing. A series of four-ball scuff tests was therefore made to find which organic sulfur compounds have antiscuffing properties. Three types of sulfur compounds (mercaptan, sulfide and disulfide), each combined with one of three different organic groups (alkyl, benzyl and phenyl), were tested at 77F in dry argon and wet air. The concentrations were 50ppm as S for mercaptans (the maximum allowable by specification) and 200ppm as S for sulfides (a typical concentration).

The results are presented in Table 10 and summarized below.

Effect Of Sulfur Compounds On Wear

	Scuff Load, kg					
	In Argon			In Wet Air		
	-SH	-S-	-SS-	-SH	-S-	-SS-
Alkyl	10	10	10	10	5	5
Benzyl	15	10	10	15	5	5
Phenyl	15	10	10	10	5	5
Base Fuel	--------5---------			--------3---------		

It will be noted that in wet air none of the sulfur compounds were effective. All gave large wear scars at 5kg, and the sulfides and disulfides also gave high friction indicative of scuffing. This is in agreement with our conclusion based on wear data: sulfur compounds in jet fuels are not responsible for differences in

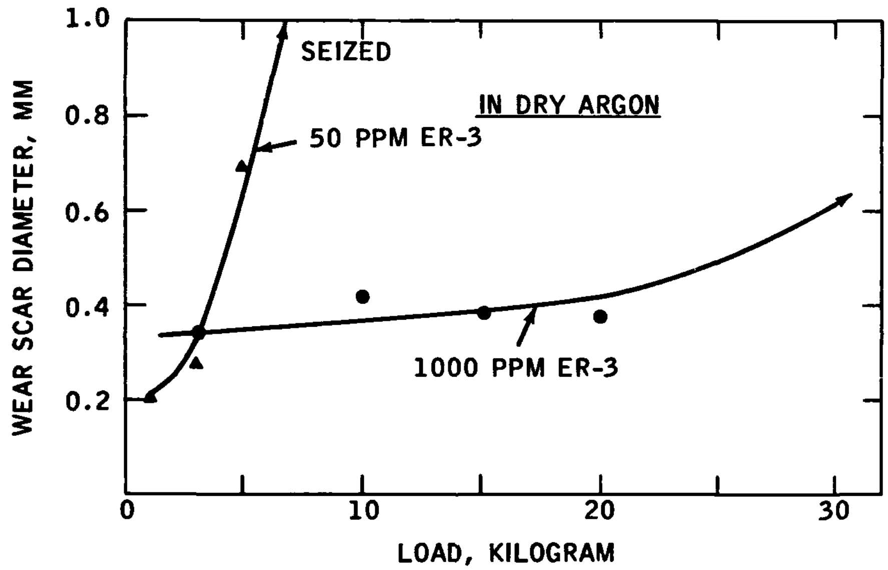


FIGURE 8 - EFFECT OF ADDITIVE CONCENTRATION (FOUR BALL TESTS - 1200RPM, 15MIN, 240F, 52100 STEEL)

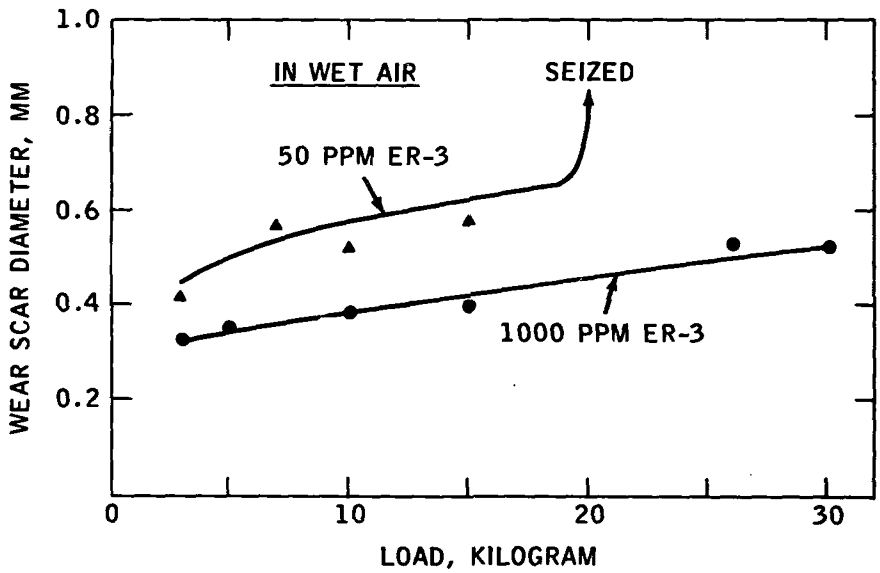


FIGURE 9 - EFFECT OF ADDITIVE CONCENTRATION (FOUR BALL TESTS - 1200RPM, 15MIN, 240F, 52100 STEEL)

TABLE 10

EFFECT OF SULFUR COMPOUNDS ON WEAR

(Four-Ball Tests, 1200rpm, 77F, 15min)

	Wear Scar Diameter, mm								Coefficient Of Friction							
	Dry Argon				Wet Air				Dry Argon				Wet Air			
Load, kg:	1	5	10	15	1	5	10	15	1	5	10	15	1	5	10	15
% Additives In PW-523																
50ppm Mercaptans,																
Octyl	0.20	0.30	S*	-	0.60	0.72	0.78	S*	0.06	0.11	***	-	0.06	0.16	0.18**	***
Benzyl	0.17	0.27	0.32	S*	0.47	0.70	0.78	0.85	0.08	0.14	0.11	***	0.07	0.14	0.16	***
Phenyl	0.20	0.27	0.29	S*	0.50	0.70	0.85	S*	0.07	0.11	0.10	***	0.07	0.17	0.33**	***
200ppm Sulfides,																
Dibutyl	0.20	0.32	S*	-	0.53	0.81	0.80	S*		0.10	***	-		0.55**	0.34**	***
Benzyl	0.18	0.31	S*	-	0.58	0.98	S*	-	0.21	0.10	***	-	0.06	0.47**	***	-
Phenyl	0.18	0.33	S*	-	0.45	0.88	S*	-	0.08	0.08	***	-	0.08	0.52	***	-
200ppm Disulfides,																
Dibutyl	0.20	0.30	S*	-	0.57	0.97	-	S*	0.15	0.09	***	-	0.08	0.51**	-	***
Benzyl	0.18	0.34	S*	-	0.58	1.00	1.02	S*	?	0.10	***	-	0.06	0.54**	0.42**	***
Phenyl	0.27	0.28	S*	-	0.57	0.72	0.92	S*	0.20	0.11	***	-	0.09	0.17**	0.28**	***
None	0.20	0.85			0.47	0.81			0.15	0.10**			0.15	0.57**		

* "S" indicates seizure.
** Erratic friction and chattering noise.
*** Friction off-scale.

lubricity observed in the field.

The data in dry argon, however, are different and are quite intriguing. All the sulfur compounds eliminated scuffing at 5kg and the wear scars were very low. Thus, these compounds are lubricity agents when oxygen and water are absent. It is possible that this finding could have practical significance. As pointed out in earlier reports, inerting the atmosphere is very beneficial in preventing corrosive wear -- as, for example, in the Vickers vane pump. However, there is always some concern that this will lead to scuffing, for we have shown that with non-ferrous metals scuffing is most severe in a dry inert atmosphere. The addition of the usual lubricity additives can reduce scuffing, but such additives are usually surfactants and can adversely affect water separation properties. Sulfur compounds probably have little effect on water separation; they could be used as mild anti-scuff compounds in an inerted system.

The behavior of these sulfur compounds also has some interesting theoretical aspects. Unlike the lubricity additives, the sulfur compounds have very little effect in wet air. Apparently their antiscuff effectiveness cannot function when water or oxygen are present. This implies either a competition for the surface between the sulfur compounds and oxygen/water (a competition which the sulfur compounds lose) or a complex reaction involving the sulfur compound, the steel surface, oxygen and water. This latter seems more likely for, as noted earlier, the sulfur compounds are pro-wear agents under non-scuffing conditions. The same effect was noted in these experiments and is summarized in the table below.

Effect Of Sulfur
Compounds On Wear At 1 kg Load

	Wear Scar Diameter, mm					
	In Argon			In Wet Air		
Sulfur Compound	-SH	-S-	-SS-	-SH	-S-	-SS-
Alkyl	0.20	0.20	0.20	0.60	0.53	0.57
Benzyl	0.17	0.18	0.18	0.47	0.58	0.58
Phenyl	0.20	0.18	0.27	0.50	0.45	0.57
Base Fuel	--------0.20--------			--------0.4[illegible]--------		

In wet air, there is a definite increase in wear particularly for the disulfides and the alkyl mercaptan.

One other peculiarity of the sulfur compounds was noted. When scuffing occurred in dry argon it was sudden and catastrophic. Friction was so high as to cause "seizure" (the overload trip to the motor would stop the test). In wet air, scuffing would occur as evidenced by high and erratic friction and a large wear scar, but "seizure" would not occur until several load increments higher. This behavior is illustrated in Figure 10.

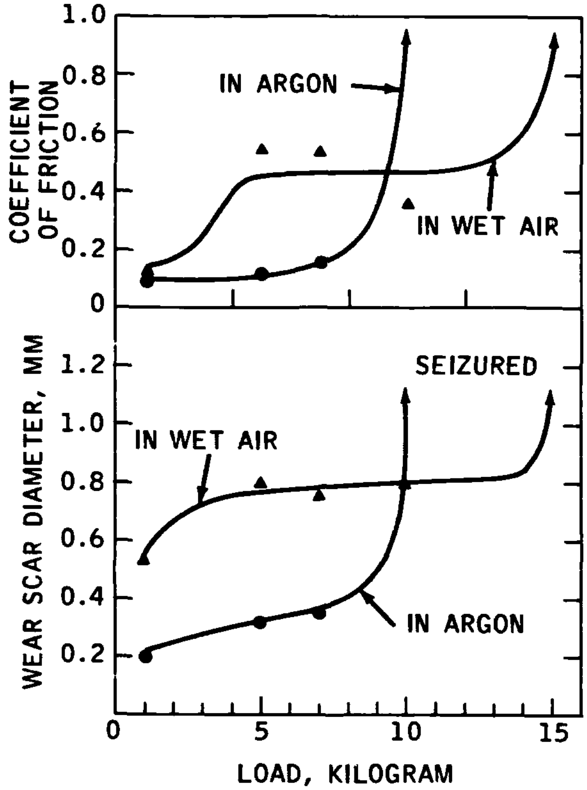


FIGURE 10 - EFFECT OF DIBUTYL SULFIDE ON SCUFFING
(FOUR BALL TESTS - 1200RPM, 15MIN, 77F)

3. <u>Olefins</u>

Olefins continue to be of interest because they can be obtained in a wide range of oxidative stability. Previous results had shown that there was some relation between oxidation tendencies and wear. To see if this relationship also held for scuffing, 5% blend of various olefins were blended in Bayol 35 and evaluated in the four-ball machine at 77F and 240F. Results are shown in Tables 11 and 12. The relative oxidation rates for these olefins were estimated by Boland's empirical rule (Boland, J. L., Trans. Faraday Soc., <u>46</u> 358-367 1950) and are shown below together with the test results in wet air at 77F.

Olefin (5% In Bayol 35)	Relative Oxidation Of Olefins	Scuff Load, kg
None	-	1
Dodecene-1	1	3
2,5 Dimethyl-2,4 hexadiene	26	15
2,5 Dimethyl-1,5 hexadiene	2.6	20
4 Vinyl-cyclohexene	350	15
α-Methylstyrene	1160	20
Allyl-Benzene	4	> 30

As before, there is a fair correlation between oxidation stability and scuffing tendencies.

There is a significant difference between isomeric olefins. As shown in the table below, changing the position of the double bonds in dimethylhexadiene from the 2,4 to the 1,5 positions caused an increase of the scuff load from 15kg to greater than 30kg. Similarly, α-methyl styrenes is inferior to its isomer, allyl benzene. In each case the molecules with conjugated double bonds were less effective than those with unconjugated bonds. That is, the less stable molecule has better lubricity.

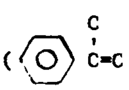
Olefins (5% In Bayol 35)	Scuff Load At 240F, kg	
	In Argon	In Wet Air
None	3	1
2-5 Dimethyl-2-4 hexadiene (C-C=C-C=C-C)	10	15
2-5 Dimethyl-1-5 hexadiene (C=C-C-C-C=C)	10	> 30
α-Methyl Styrene ()	10	15
Allyl Benzene ( C-C=C)	30	> 30

TABLE 11

EFFECT OF OLEFINS ON WEAR

(Four-Ball Tests, 1200rpm, 77F, 15min)

	Wear Scar Diameter, mm												Coefficient Of Friction											
	Dry Argon						Wet Air						Dry Argon						Wet Air					
Load, kg:	5	10	15	20	25	30	5	10	15	20	25	30	5	10	15	20	25	30	5	10	15	20	25	30
Olefin (5wt%) In Bayol 35																								
None	0.28	S*					0.78**						0.09	***										
Allyl Benzene	0.32	0.33	0.36	0.34	0.47	S*	0.48	0.48	0.49	0.53	0.60	0.68	0.14	0.12	0.10	0.11	0.13	***	0.18	0.15	0.15	0.14	0.13	0.12
α-Methyl Styrene	0.29	0.25	S*	-	-	-	0.49	0.49	0.56	S*	-	-	0.11	0.10	***	-	-	-	0.13	0.11	0.10	***	-	-
2-5 Dimethyl-2-4 hexadiene	0.23	0.31	S*	-	-	-	0.47	0.51	S*	-	-	-	0.11	0.11	***	-	-	-	0.16	0.13	***	-	-	-
2-5 Dimethyl-1-5 hexadiene	0.27	0.28	0.35	S*	-	-	0.37	0.42	0.45	0.48	S*	-	0.13	0.10	0.10	***	-	-	0.17	0.16	0.15	0.15	***	-
Vinyl Cyclohexene	0.27	0.28	S*	-	-	-	0.43	0.48	S*	-	-	-	0.11	0.10	***	-	-	-	0.18	0.15	***	-	-	-

* "S" indicates seizure.
** Scuffed at 6kg load.
*** Friction off-scale.

TABLE 12

EFFECT OF OLEFINS ON WEAR

(Four-Ball Tests, 1200rpm, 240F, 15min)

	Wear Scar Diameter, mm												Coefficient Of Friction											
	Dry Argon					Wet Air							Dry Argon					Wet Air						
Load, kg:	3	5	10	15	30	3	5	10	15	20	25	30	3	5	10	15	30	3	5	10	15	20	25	30
Olefin (5wt%) In Bayol 35																								
None	0.71					S*												**						
Allyl Benzene	0.25	0.30	-	0.43	0.47	0.23	0.47	-	0.52	0.60	0.53	0.62	0.15	0.1	-	0.13	0.12		0.11		0.15	0.15	0.15	0.12
α-Methyl Styrene	0.25	0.30	S*		-		0.45	0.67	0.63	S*	-	-	0.12	0.13	**	-	-		0.14	0.13	0.13	**	-	-
2-5 Dimethyl-2-4 hexadiene	0.27	0.30	S*		-	0.52	0.57	0.70	S*	-	-	-	0.13	0.11	**	-	-		0.13	0.13	**	-	-	-
2-5 Dimethyl-1-5 hexadiene	0.27	0.30	S*		-	0.42	0.48	0.60	0.67	0.58	0.70	0.77	0.11	0.10	**	-	-	0.15	0.14	0.15	0.14	0.14	0.14	0.15
Vinyl Cyclo-hexane	0.27	0.28	S*		-	0.44	0.67	0.60	S*	-	-	-	0.16	0.13	**	-	-	0.15	0.16	0.12	**	-	-	-

* "S" indicates seizure.
** Friction off-scale.

A more detailed comparison of the test results for 5% α-methyl styrene and allyl benzene is shown in Figure 11.

At higher temperatures the fuels containing olefins do not show as much decrease in scuff load as the base fuel. This is presumably because the less-stable molecules are more reactive at higher temperature. In air, the olefin blends are at least as good at 240F as at 77F, indicating that fuel oxidation has counteracted the adverse effects of temperature. These data are summarized below.

Four-Ball Scuff Loads

	In Argon		In Wet Air	
	77F	240F	77F	240F
None	10	3	6	1
5% $C{-}\overset{\vert}{C}{=}C{-}C{=}\overset{\vert}{C}{-}C$	15	10	15	15
5% $C{=}\overset{\vert}{C}{-}C{-}C{-}\overset{\vert}{C}{=}C$	20	10	25	30
5% α-Methyl Styrene	15	10	20	20
5% Allyl Benzene	25	> 30	> 30	> 30

Thus the demand for fuels of better thermal stability has had two undesirable effects so far as lubricity is concerned. The refining process removes the unstable molecules (such as olefins) which are fair lubricity agents. It also removes the heavy aromatics which are both good in lubricity and stable toward oxidation. The most stable fuel would be one from which all polar molecules were removed and then the heavy aromatics added back. However, from a practical point of view it would probably be cheaper to use lubricity additives rather than aromatics.

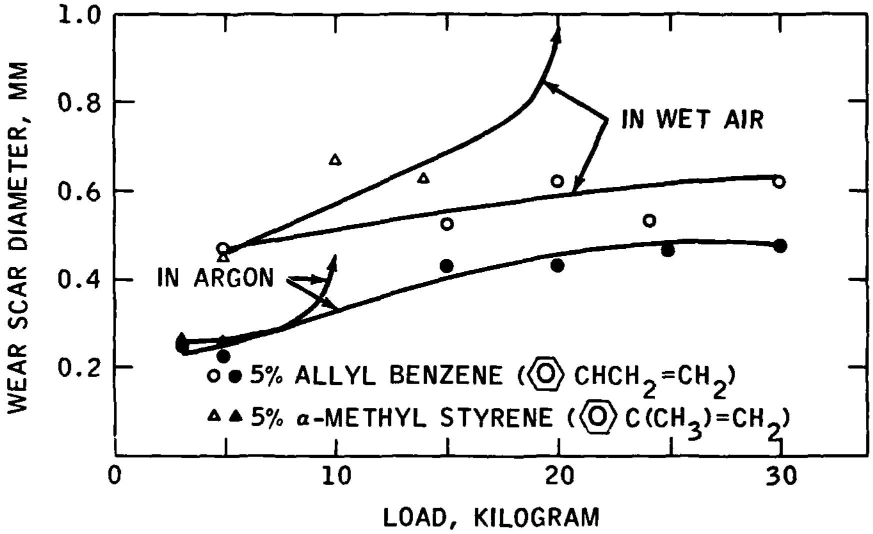


FIGURE 11 - COMPARISON OF SCUFFING LOAD BETWEEN
α-METHYL STYRENE AND ALLYL BENZENE
(FOUR BALL TESTS - 1200RPM, 15MIN, 240F)

IV. PUBLICATIONS

Two new papers have been prepared and submitted for publication:

"The Lubricity Characteristics Of Heavy Aromatics" by J. K. Appeldoorn and F. F. Tao to be presented at the ACS Petroleum Division, Symposium on the Chemistry of Lubrication, San Francisco, April 1-5, 1968.

"The Ball-On-Cylinder Device For Measuring Jet Fuel Lubricity" by F. F. Tao and J. K. Appeldoorn, to be presented at the ASLE Annual Meeting, Cleveland, May 6-9, 1968.

Prepared comments were also presented on two papers at the ASLE-ASME Joint Lubrication Conference, Chicago, October, 1967.

V. FUTURE WORK

The final work to be done under this contract will be as follows:

- Complete work on the nature of wear and scuffing in both ferrous and non-ferrous metallurgies.
- Define the nature of corrosive wear and write a paper for publication on this subject.
- Broaden the mathematical treatment of the role of diffusion in corrosive wear to take into account the rate of formation and rate of breakoff of the oxide layer.